

PATENT APPLICATION

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re application of

KITAMURA et al

Appln. Serial No.: 09/281,809

Group Art Unit: 1774

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Examiner: M. Grendzynski

For: INK JET RECORDING MATERIA AND PRODUCING PROCESS THEREOF

DECLARATION UNDER 37 C.F.R. §1.132

Commissioner for Patents  
Washington, D.C. 20231

Sir:

I, Ryu Kitamura, a citizen of Japan, residing at Art Homes  
Bldg.106, 23-5, Masago 2-chome, Mihama-Ku, Chiba-shi,  
Chiba, Japan, do hereby declare as follows.

I graduated from Osaka City University, Faculty of Human  
Life Science, in March, 1992, and hold a degree of Doctor  
Philosophy, from Osaka City University, obtained through a  
study concerning Environmental Design.

Since April 1992, I have been continuously employed by  
OJI PAPER CO., LTD.

Since April 1992, I have been engaged in research at the  
Imaging Media Development Laboratory.

*Handwritten signature/initials*

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I am a co-inventor of the invention of the above-captioned U.S. patent application, presently outstanding, with respect to an ink jet recording material.

I am thoroughly familiar with the constitution and production of ink jet recording material because I have been closely involved, during the past several years, in the evaluation of domestic and international patents and patent applications concerning ink jet recording material.

I have reviewed the Office Action of November 30, 2001 regarding the above application and have noted the Examiner's allegation that claims 1-5, 7-18 and 23-26 of the present application would be rendered obvious over Miyamoto et al (U.S. Patent 4,460,637) and/or Asano et al (U.S. Patent 5,670,242).

In order to demonstrate the unexpected effect and the superiority of the present invention over the references, the following comparative experimentation was carried out.

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- Comparative Experimentation -

Comparative Example 1:

The comparative sample 1 of ink jet recording material was prepared in the same manner as in Example III-1 of U.S. Patent 5,670,242 (Asano et al), as follows.

An undercoating liquid having a solid content of 15% was prepared by using 100 parts of amorphous silica (pigment), 20 parts of polyvinyl alcohol (adhesive), 5 parts of a polyethylenepolyamine-dicyandiamide-ammonium salt polycondensation product (cationic resin; "PNF-70" (trade name), made by Nikka Kagaku Kogyo K.K.) and 0.5 part of sodium polyphosphate (dispersing agent). The undercoating liquid was applied at a dry coating rate of 10 g/m<sup>2</sup> by an air knife coater onto a base paper having a basis weight of 100 g/m<sup>2</sup> to prepare an undercoated base paper, which showed a Gurley air permeability of 4 sec/10cc.

On the other hand, a cast-coating liquid having a solid content of 35% was prepared by using 50 parts of styrene-2-methylhexyl acrylate copolymer having a glass transition point (T<sub>g</sub>) of 80 °C., 50 parts of colloidal silica and 2 parts of calcium stearate (release agent). The cast-coating liquid was applied by a roll coater onto the above-prepared undercoated base paper to form a wet cast-coating layer, which was immediately thereafter pressed against a mirror-finished drum having a surface temperature of 75 °C, to be dried,

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followed by releasing, to form a cast coated paper for ink jet recording. The coating rate (solid) at this time was  $5 \text{ g/m}^2$ . The cast coated paper showed an air permeability (according to JIS-P-8117) of 50 sec/100 cc.

In preparation of the sample, since silica, PVA and colloidal silica were not described in Example III-1, the following commercially available ones were used.

Silica: the amorphous silica having an average particle size of  $6.0 \mu\text{m}$  ("Finesil X-60" manufactured by Tokuyama K.K.) was used.

PVA: PVA-117 (polymerization degree: 1700, saponification degree: 98.5%); manufactured by Kuraray CO.) was used.

Colloidal Silica: the colloidal silica having an average primary particle size of 45 nm ("ST-20 L" manufactured by Nissan Chemical Industries, Ltd.) was used.

Support: the commercially available coated paper ("OK coat"  $127.9 \text{ g/m}^2$ ; manufactured by OJI PAPER CO., LTD.) was calender-treated and then used.

#### Comparative Example 2:

The comparative sample 2 of ink jet recording material was prepared in the same manner as in Example 1 of U.S. Patent 4,460,637 (Miyamoto et al), as follows.

According to the procedure disclosed in detail in U.S. Patent No. 3,855,172, Example 1, a granular pigment was prepared as by granulating colloidal silica of 40 m $\mu$  in particle size ("Snowtex OL" of Nissan Chemical Co.) with a urea resin as binder, and roasting the granules to yield spherical agglomerates of 10  $\mu$ m in size. A coating composition of 20% solids content was prepared by mixing 100 parts of the above pigment agglomerates and 15 parts of polyvinyl alcohol ("PVA 117" of Kuraray Co.) as an adhesive.

The coating composition was coated on the corona discharge treated surface of a piece of polyethylene terephthalate film at a coverage of 15 g/m<sup>2</sup> on dry basis and drying to form an ink receptive layer on the support of polyethylene terephthalate.

Also, as the support, the commercially available coated paper ("OK coat" 127.9 g/m<sup>2</sup>; manufactured by OJI PAPER CO., LTD.) was calender-treated and then used.

Comparative Example 3:

The comparative sample 3 of the ink jet recording material was prepared by adding to the coating solution of the above Comparative Example 2 further 5 parts of the cationic resin, polyethylenepolyamine described in Example III-1 of Asano et al ("PNF-70" manufactured by Nikka Kagaku Kogyo K.K.).

Also, as the support, the commercially available coated paper ("OK coat" 127.9 g/m<sup>2</sup>; manufactured by OJI PAPER CO., LTD.) was calender-treated and then used.

Example 1:

100 parts of colloidal silica ("Snowtex OL" made by Nissan Chemical Co.) having an average particle size of 40nm described in Example 1 of Miyamoto et al (provided that is not coagulated), 10 parts of polyvinyl alcohol ("PVA-117" made by Kuraray Co.; polymerization: 1700; saponification degree: 98.5%) described in Example 1 of Miyamoto et al were mixed to obtain 15% aqueous solution.

Then, to the obtained 15% aqueous solution, 3 parts of the cationic resin, polyethylenepolyamine ("PNF-70" made by Nikka Kagaku Kogyo K.K.) described in Example III-1 of Asano et al was gradually added while dispersing, and then was again dispersed.

The dispersed mixture was coated on the commercially available coated paper in a coated amount of 15 g/m<sup>2</sup> by using a mayer bar, and then dried to prepare the sample of an ink jet recording material according to the present invention.

The obtained samples of ink jet recording materials were evaluated by the following evaluation method.

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[Evaluation]

The pore diameter distribution of the ink jet recording paper sheets obtained in Example 1 and Comparative Examples 1 to 3 were measured by the method described in the present specification. The water resistance, water absorption, etc. of these ink jet recording paper sheets were evaluated by the methods described below. For the evaluation of gloss and ink absorption, recording was conducted on these ink jet recording paper sheets by means of a commercial ink jet printer (BJC-600J, available from Canon Inc.). The gloss, ink absorption and print density on the solid area were then measured.

[Water resistance]

A water droplet was dropped onto the ink jet recording sheet. After 30 minutes, the water droplet was wiped off the sheet. The sheet was then rubbed with a hand on the area impregnated with water. The water resistance was evaluated according to the following four-set criterion.

- ◎: No change is observed on the ink-receiving layer;
- : Ink-receiving layer is slightly peeled off;
- △: Ink-receiving layer is partly peeled off; and
- ×: Ink-receiving layer is entirely peeled off.

[Ink absorption]

For the evaluation of ink absorption, a wood paper was applied to the printed surface of the ink jet recording material every 5 seconds shortly after printing to see whether or not the ink was transferred to the woodfree paper. The time required until no ink is transferred to the woodfree paper was determined. The ink adsorption was then evaluated according to the following four-step criterion.

- ⊙: No more than 5 seconds;
- : 5 to 10 seconds;
- △: 10 to 30 seconds; and
- ×: Not less than 30 seconds.

[Print density]

The ink jet recording material was measured for print density on the black solid area by means of a Macbeth reflection densitometer (Macbeth, RD-920). The figure shown in the table below is the means of five measurements.

[Gloss (luster) on the printed area]

For the evaluation of the gloss on the printed area, the printed area was visually observed at a horizontal angle of 20°. The gloss on the printed area was evaluated according to the following four-step criterion.



- ◎: Same level of luster as color photograph is felt;
- : Luster inferior to color photograph but still high is felt;
- △: Luster as high as printed coated paper is felt; and
- ×: Luster as high as ordinary PPC is felt.

Also, the pore diameter distribution was measured by the following method for the obtained samples.

The measurement of pore diameter distribution will be described hereinafter.

In the present invention, in order to minimize the effect of the support, the ink-receiving layer was formed on a polyester film ("Lumirror T" available from Toray Industries, Inc.; 75  $\mu$  m) to give a specimen to be measured.

For the measurement of pore diameter distribution, Poresizer 9320 (available from Shimadzu Corp.) was used. The pore diameter distribution (differential curve) can be obtained from a void distribution curve determined by mercury intrusion method.

In the measurement of pore diameter by mercury intrusion method, the pore diameter was calculated by the following equation derived on the assumption that the section of pore is circular:

$$D = -4 \gamma \cos \theta / P$$

wherein D is a pore diameter,  $\gamma$  is a surface tension of mercury,  $\theta$  is a contact angle, and P is a pressure.

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The surface tension of mercury was set to 484.536 dyne/cm. The contact angle used was 130°. Under these conditions, mercury pressure was measured at a low pressure portion (0 to 30 psia; pore diameter to be measured: 360  $\mu\text{m}$  to 6  $\mu\text{m}$ ) and a high pressure portion (30 to 30,000 psia; pore diameter to be measured: 6  $\mu\text{m}$  to 6 nm). The average pore volume of the ink-receiving layer is calculated from the weight of the ink-receiving layer previously measured and the void distribution curve. In the present invention, once the pore diameter distribution curve of the various layers containing primary colloidal particles has shown peaks lying in the range of from 6 nm to 100 nm, the measurement is finished.

If there were recognized no peaks in the range of from 6 nm to 100 nm, ASAP 2010 (high speed specific surface area/pore diameter distribution measuring instrument available from Shimadzu Corp.; gas absorption method by constant volume method), which can measure pore diameters of from 1 nm to 100 nm, was used to continue measurement.





With proviso that the measurement of the pore diameter distribution was carried out by shaving the coated layer.

The results of the above evaluation and measurement are shown in Table A below.

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TABLE A

	<u>Ink absorp- tion</u>	<u>Water resis- tance</u>	<u>Print density</u>	<u>Gloss on printed area</u>	<u>Peak of pore diameter distri- bution</u>	<u>Dot Shape</u>
Comparative Example 1	○	◎	1.65	×	10 nm 3 μ	
Comparative Example 2	◎	◎	1.30	×	10 nm 0.9 μ	
Comparative Example 3	◎	◎	1.54	×	8 nm 0.9 μ	
Example 1	◎	◎	2.21	○	12 nm	



: bleeding cloud



: Pebble-like



: Round (i.e., circle)

As is apparent from the results of Table A, the dot shape is controlled to the round and the definitive image can be obtained, by controlling the peak of pore diameter distribution to from 2 to 100 nm.

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Therefore, it is believed that the unexpected effect of the present invention and the superiority of the present invention over the references are demonstrated from the results of Table A.

I declare further that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issuing thereon.

Date : March 15, 2002

Name : Ryu Kitamura  
Ryu Kitamura